SPECTROSCOPIC INVESTIGATIONS OF THE FORMATION
OF THE Zn-Sn-O NANOSTRUCTURED FILMS

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The aim of this work is to obtain nanostructured Zn-Sn-O films by sol-gel method. Stable solutions with Sn/Zn atomic ratio of 1:1 and 1:2 of zinc and tin, respectively, were obtained starting from Sn(II) 2- ethylhexanoate and zinc acetate dehydrate in ethylic absolute alcohol and triethanolamine. Solutions which contain both tin and zinc cations exhibit fluorescence emission even after four days storage. The obtained powders are amorphous. Mono- and multi-layer films were deposited on glass and silicon substrates. A beginning of crystallization of Zn_2SnO_4 can be seen by XRD in the case of films with Sn/Zn atomic ratio of 1:2. The surface topography of the films was estimated by AFM. The refractive index values in the 1.6-2.3 range were calculated from Spectroellipsometry data using Cauchy Model. Fluorescence emission was observed in the case of studied films excepting tin dioxide. The structure, morphology and optical properties of the obtained films depend on the composition, number of deposition and the thermal treatment temperature.

INTRODUCTION

In recent years, there have been extensive studies on thin films exhibiting high electrical conductivity as well as high transparency in the visible spectral range and high reflectivity in the IR spectrum. ZnO and SnO_2 films have been two of these transparent conductive oxides (TCOs), which are widely used in many optoelectronic devices as transparent and conducting coatings. Although for these applications the TCO films of In_2O_3:Sn (ITO), SnO_2:F or SnO_2:Sb (FTO or ATO) and ZnO:Al (AZO) are already established and are obtained at industrial scale, the growing demands for improved performance and lower cost of opto-electronic devices have resulted in an effort to develop new alternative TCO materials to replace the commercial ones.[1] These new TCOs include binary and multicomponent metal oxides of Zn, Cd, Sn and In with various additives.

Among the most promising materials proposed for future research are $ZnSnO_3$ and Zn_2SnO_4 binary oxide compounds. Thin zinc stannate ($ZnSnO_3$) films have been recently considered as promising candidates for optoelectronic devices and gas sensor due to their large optical band gap (Eg-3.6 eV), high optical transmittance and resistance to the environment effects.[2] Highly transparent and conductive ZnO, SnO_2, $ZnSnO_3$ films have been deposited using various deposition techniques, including spray pyrolysis, sol-gel,[3-5] magnetron sputtering,[6] and filtered vacuum arc deposition.[7]

Cetinorgu[7] obtained ZnO, SnO_2 and zinc stannate films, by filtered vacuum arc deposition having their refractive index and the extinction coefficient in the range of 1.87-2.15 and 0.02-0.04,

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respectively, depending on wavelengths and deposition parameters.

The binary oxide compounds like Cd_2SnO_4, $ZnSnO_3$, Zn_2SnO_4, $ZnGa_2O_4$ and $GaInO_3$ were mentioned in the literature data for TCO coatings obtained by different methods.[8-10]

In the literature data there are few references about sol-gel deposition of the thin films such as Cd_2SnO_4,[11-12] $ZnGa_2O_4$,[13] In_6WO_{12}[14] and Zn_2SnO_4.[15] Thick-film sensors, around 500 nm, were obtained using Zn_2SnO_4 particles prepared by the sol-gel method.[16]

Kurz and Aegerter[17] obtained films on borosilicate glass and fused silica substrate with thicknesses of up to 230 nm starting from solutions prepared by combinatorial chemistry with a robotic sample processor using different Zn(II), Sn(II) and Sn(IV) salts and alkoxides, as well as salts of different doping agents [*e.g.* Sb(V), Ta(V), In(III)] dissolved in various solvents and additives. In the concentration range of $0.4 < [Zn]/([Zn] + [Sn]) < 0.75$ except for a few cases mixed crystalline phases of ZnO, SnO_2 and $ZnSnO_3$ or Zn_2SnO_4 are usually observed. Pure sol gel Zn_2SnO_4 and $ZnSnO_3$ coatings exhibit good optical properties, but high resistivity of $\rho > 3$ Ωcm was observed unlike the similar coatings obtained by sputtering and pulsed laser deposition.

This work aims to obtain nanostructured powders and films in the Zn-Sn-O system by sol gel method. This paper presents the results obtained in the Zn-Sn-O system for Sn/Zn atomic ratio of 1:1 and 1:2.

EXPERIMENTAL

The starting materials (all reagent grade) for obtaining precursor solutions are the following: Sn(II)2-ethylhexanoate–$Sn(C_7H_{15}COO)_2$ (SIGMA), zinc acetate dehydrate-$Zn(CH_3COO)_2 x2H_2O$, absolute ethanol-CH_3CH_2OH (Merck) and triethanolamine-$(CH_3CH_2OH)_3N$ (BAKER ANALYZED). Solutions with Sn/Zn atomic ratio of 1:1 and 1:2 and 0.1M concentration were obtained in absolute ethanol using as chelating agent triethanolamine (TEA) for molar ratio precursor/TEA =5:1.

The prepared solutions were stirred at 50°C for 120 minutes and were identified by abbreviation: T-S for tin solution; TZ-S for tin and zinc solution with atomic ratio of 1:1; TZ_2–S for tin and zinc solution with atomic ratio of 1:2 and Z-S for zinc solution. The gels were obtained from the solutions used for films deposition by solvent evaporation in air, at room temperature.

Powders, abbreviated T-P; TZ-P; TZ_2–P and Z-P, resulted after the thermal treatment at 500 °C temperature one hour of the gels.

The prepared solutions were stored at room temperature 24 hours before deposition by dip-coating technique on glass and silicon substrates for obtaining the films of interest.

The deposition conditions were: withdrawal speed 5 cm/min, withdrawal temperature 20 ºC and the number of depositions 1-4. Based on DTA/TG results of as prepared gels, the obtained films were thermally treated at 500 ºC for 5 min after each deposition and the final thermal treatment was realized also at 500 ºC but for one hour.

The films were labeled as follows: TZ–$F_{S,G}$, for Zn-Sn-O films with Zn/Sn initial atomic ratio =1:1; TZ_2-$F_{S,G}$, for Zn-Sn-O films with Zn/Sn initial atomic ratio =2:1; where S - silicon and G-glass substrates; TZ-F_{unc} and TZ_2-F_{unc}, for as prepared films; TZ-$F_{S,G_{nT}}$ and TZ_2-$F_{S,G_{nT}}$, for thermally treated films where n=1, 2, 3, 4 is the number of depositions.

The evolution of the solutions was observed by Fluorescence Spectroscopy with Perkin Elmer 204 spectrofluorimeter (with a Xe lamp of 150 W), interfaced to a computer, permitting a prestabilized reading time of the data. Usually the time range between two measurements is 550 ms. The spectral measurements (fluorescence emission spectra) were performed at room temperature.

The obtained gels were investigated by DTA and TG/DTA with a Mettler Toledo TGA/SDTA 851^e equipment in the 20-1000 °C temperature range with a heating rate of 5^{0}C/min and by FT-IR Spectroscopy with a Nicolet 6700 apparatus in 400-4000 cm^{-1} domain.

XRD analysis of the films was performed with Rigaku Ultima IV diffractometer, Cu Kα X-ray radiation, $\lambda = 1.5406$ Å. The powder diffraction patterns were obtained by continuous scanning with scan speed of 5 degrees· min^{-1} and step width of 0.02 degrees from $2\theta = 10°$ to 80°.The X-ray tube was operated at 40 kV and 30 mA.

The surface morphology (grain size and surface roughness) was analyzed by Atomic Force Microscopy (AFM). The AFM experiments were carried out in the intermittent contact mode, with an EasyScan2 apparatus (Nanosurf® AG, Switzerland). Topography and phase contrast working modes were used for imaging by means of a 10 μm x 10 μm high resolution scanner; with a scan rate around 1-2 Hz. All AFM measurements have been performed with sharp tips (PPP-NCLR type from Nanosensors™). The AFM image analysis was carried out based on Scanning Probe Image Processor - SPIP™ (v. 4.6.0) software procedures to determine the Root-Mean-Square (RMS) surface roughness and to evaluate the dimensions of the superficial grains.

The optical properties were determined by Spectroellipsometric (SE) measurements and Fluorescence Spectroscopy. Spectroellipsometric measurements were performed with a Variable Angle Spectroscopic Ellipsometer (VASE) from J.A. Woollam Co. in the spectral range of 300 – 800 nm. Fluorescence measurements were performed with the apparatus mentioned for solutions.

RESULTS AND DISCUSION

1. Solutions

Transparent, stable over ninety days, yellowish solutions were used to obtain ZnO, SnO_2 and Zn-Sn-O materials (Zinc/Tin atomic ratio 1:1 and 2:1). The atomic ratios were selected in order to obtain $ZnSnO_3$ and Zn_2SnO_4 compounds.

The evolution of the solutions during the storage was observed by Fluorescence Spectroscopy.

Fig. 1 presents the fluorescence emission spectra of the Zinc solutions (Z-S) stored at room temperature for four days (Z-S1 – Z-S4). As can be seen, using an excitation wavelength of 270 nm, the fluorescence emission spectra have one structured emission band at about 308 nm. The zinc solution (Z-S) initially presents a weak fluorescent signal, which increases by storage of the solution at room temperature. No change in the maximum emission wavelength is observed. The fluorescence intensity increases through three days storage at room temperature probably due to the formation of hydrogen bonds in the presence of triethanolamine. The fluorescence emission is quenched after four days storage of the Z-S solution at room temperature, being almost nine times lower than the value of the as prepared Z-S solution. Moreover, the fluorescence emission wavelength is 3 nm red-shifted, facts that could be attributed to the coordination of zinc ions with triethanolamine.

Table 1 shows the fluorescence parameters of the TZ-S and TZ_2-S solutions; their Sn:Zn molar ratio is 1:1 and 1:2, respectively.

Unlike Z-S solution, for TZ-S and TZ_2-S solutions a continuous increase of the relative fluorescence intensity even after four days of storage was observed. The origin of the fluorescence emission of the analyzed Zn-Sn-O solutions needs more investigation and this topic should be developed in further study.

2. Powders

The gels obtaining after removal of the solvent at room temperature, from T-S, TZ-S, TZ_2-S and Z-S solutions were analysed by DTA/TG analysis in the $20\text{-}1000^0C$ temperature range. The DTA curves are shown in Fig. 2.
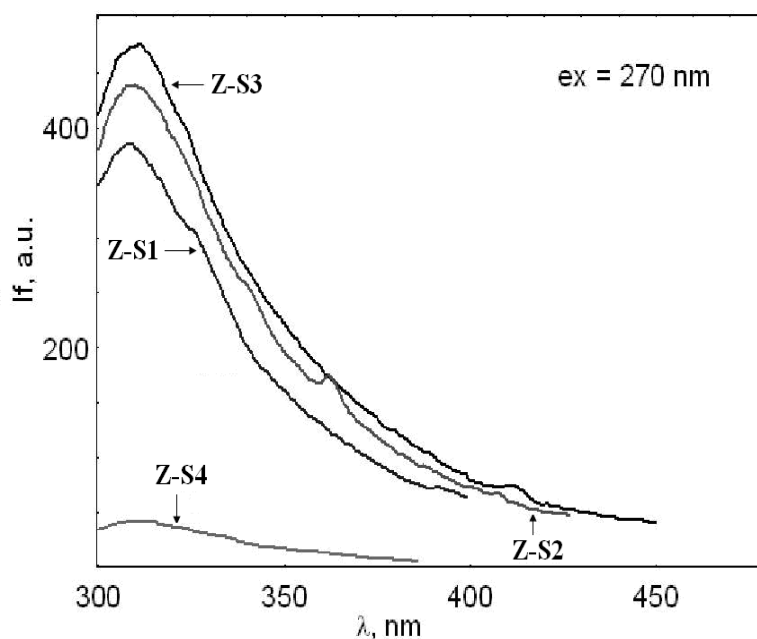

Fig. 1 – The fluorescence emission spectra of the Zinc solutions (Z-S) stored at room temperature for four days (Z-S1 – Z-S4).

Table 1

The fluorescence emission maximum, λ_{em}, and the relative fluorescence intensities, If, of the TZ-S and TZ_2-S stored for 1-4 days at room temperature; λ_{ex} =350nm

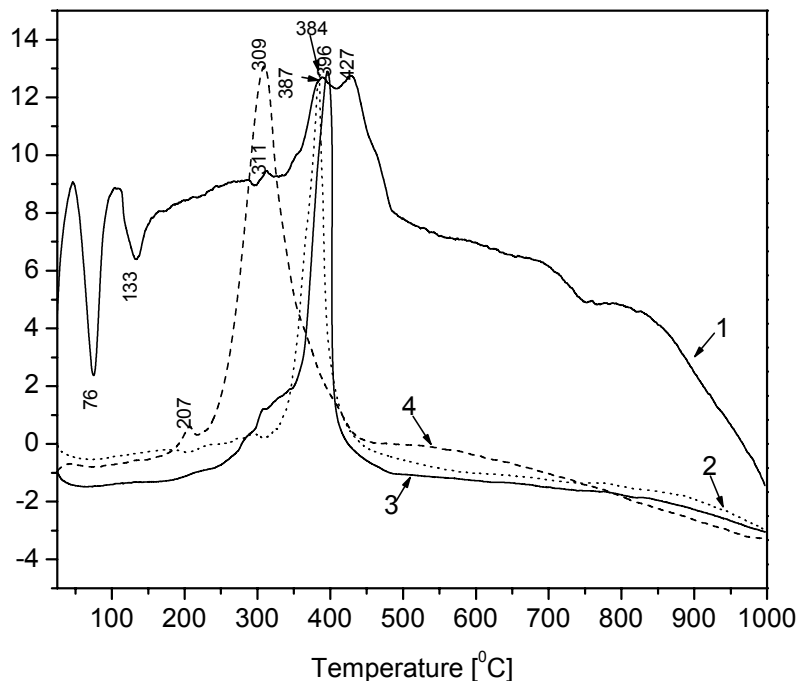| Sample	Storage period	λ_{em} (nm)	If (a.u.)
TZ-S	1 day	405,99	35,64
TZ_2-S		412,50	49,00
TZ-S	2 days	410,80	59,90
TZ_2-S		415,52	76,73
TZ-S	3 days	411,84	74,13
TZ_2-S		416,08	96,95
TZ-S	4 days	412,17	126,73
TZ_2-S		413,80	167,32

Fig. 2 – DTA curves of the gels: 1-Zn-O gel; 2-TZ$_2$-O gel; 3-TZ-O gel; 4-T-O gel.
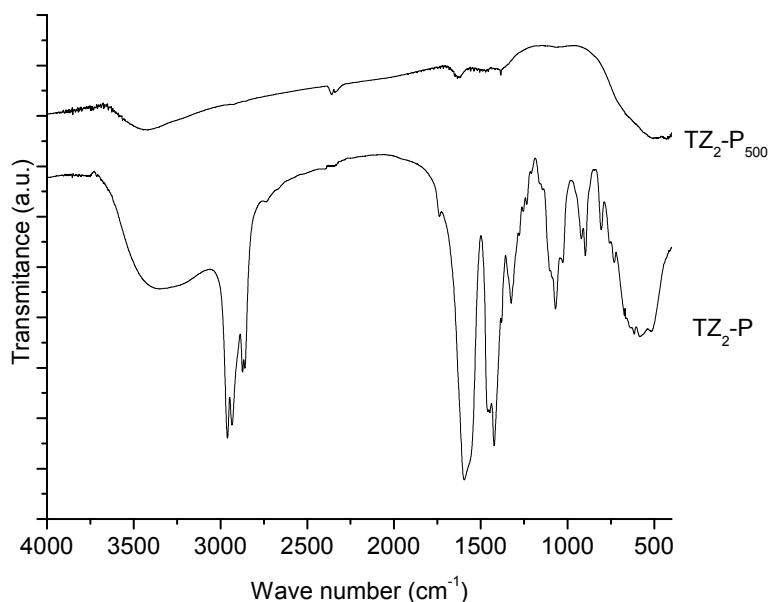

Fig. 3 – FT-IR spectra of the TZ$_2$ dried gel and of the TZ$_2$–P powder obtained after thermal treatment for one hour at 500^{0}C.

Thermal analysis of the Z-dried gel indicates that the total elimination of the organic component occurs at a temperature with 80°C higher than the one of zinc acetate (427 ºC against to 347 ºC) [17]. The TZ and TZ$_2$ dried gels present a similar thermal behavior. The main decomposition effect of the binary gel lies between the decomposition effect of the mono component ones (309 ºC and 427 ºC respectively) leading to the conclusion that in the case of the binary system not a mixture of phases occurs, but a complex gel is formed.

In the Fig. 3 FT-IR spectra of the TZ$_2$-dried gel and of the of TZ$_2$–P powder obtained after thermal treatment for one hour at 500^{0}C are presented.

FT-IR spectrum of the dried gel shows characteristic bands of O-H stretching at 3000-3500 cm^{-1} and adsorbed water in the 1600 cm^{-1} region, the carboxylate bands (asymmetric and symmetric stretching of C=O, respectively) in the 1400-1580 cm^{-1} and vC-C of organic salts at 1070 cm^{-1}.

In FT-IR spectrum of the powder, thermally treated at 500 ºC only the broad absorption bands of the metallic oxide network are observed.

3. Films

3.1. Characterization of the Zn-Sn-O films with zinc/tin ratio 1:1

XRD diffraction performed on the TZ-F_{S4T} film (zinc/tin ratio 1:1), deposited on the silicon substrate underlined its poor crystallinity. The spectrum is presented in the Fig. 4 along with the characteristic diffraction lines from ASTM files for ZnO (79-0208), SnO$_2$ (77-0448) and ZnSnO$_3$ (11-0274).

The broad and week peaks at 34 and 55 degrees indicate the formation of the Zn$_2$SnO$_4$ nuclei, no ZnSnO$_3$ compound, although Kurz and Aegerter[17] for the same composition starting from ZnCl$_2$ and Sn(O^{i}Pr)$_4$ reported week diffraction lines for ZnSnO$_3$. The same behaviour, previously published[18-19] was observed in the case of the phase formation by solid state reactions.

The sharp diffraction line of about 51 degrees could be assigned to the silicon substrate according to ASTM file (72-1088).

In Fig. 5 (a and b) AFM images in the 3D (tri-dimensional) topographic representation of the thermally treated films after four layers deposition on the glass (TZ-F_{G4T}) and silicon (TZ-F_{S4T}) substrates are presented. For comparison reasons, all AFM images in this paper have been reported in 3D view at a scale of 4μm x 4μm.

As can be seen in Fig. 5 (a and b), the TZ-$F_{S,G4T}$ films obtained in the conditions previously presented are adhesive (no exfoliations), continuous, homogenous and very smooth (with RMS roughness values of less that 1 nm). It can be seen that the roughness of the coating deposited on silicon is two times lower than the roughness of the coating deposited on glass. The results agree closely with the previous work of Yoldas[20] showing that more ordered substrate leads to lower roughness of the coatings deposited on them.

The average grain size calculated by AFM for TZ-$F_{S,G4T}$ films deposited on the glass and silicon substrate is presented in Table 2.

It can be observed that the average grain size is significantly smaller in the case of the TZ-F_{S4T} film (on the silicon substrate) then of the TZ-F_{G4T} film (on glass substrate). The grain width is estimated to be around 62 nm for the films deposited on the glass substrate and 6.3 nm for the films deposited on silicon substrate.
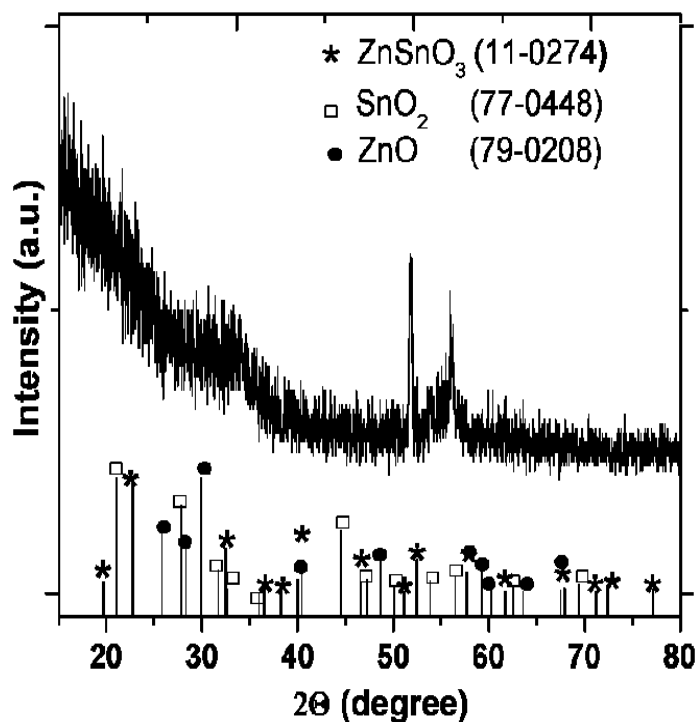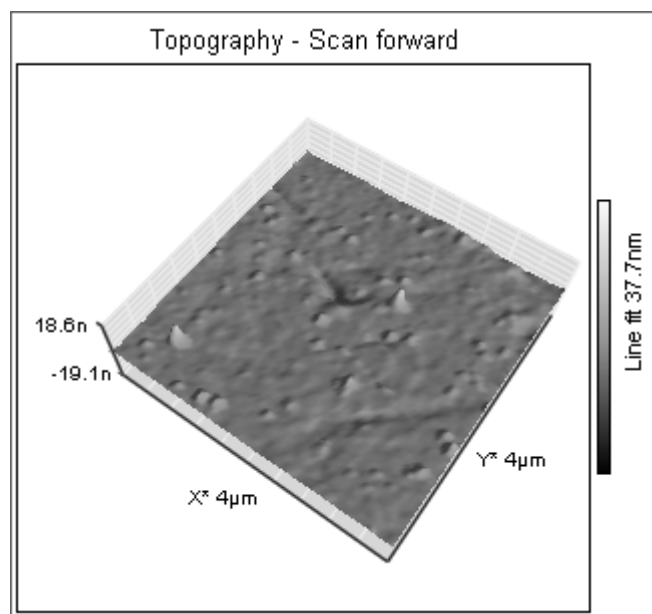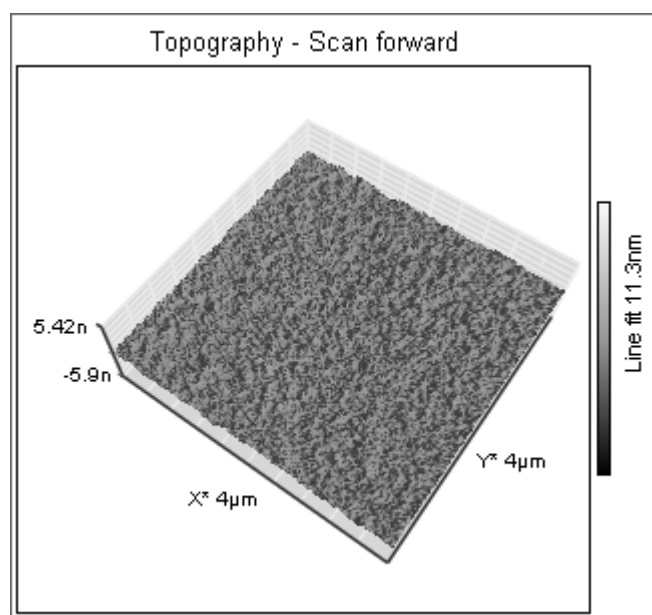

Fig. 4 – XRD pattern of Zn–Sn–O film with zinc/tin ratio 1:1, deposited on silicon substrate.

a) RMS = 0.61 nm

(b)

RMS = 0.28 nm

Fig. 5 – 3D AFM images of the TZ-F$_{4T}$ films: (a) deposited on glass substrate (RMS= 0.61 nm);
(b) deposited on silicon substrate (RMS=0.28 nm).

Table 2

Grain sizes of the TZ-F$_{4T}$ type films deposited on glass and silicon substrate; (L-length; W-width; D- diameter)

	Glass support			Silicon support		
ID	L(nm)	W(nm)	D(nm)	L(nm)	W(nm)	D(nm)
Mean	187	62	120	17	6	11
SD	152	36	80	5	2	3

Table 3

The thickness of TZ-F type films

Films	Thickness (nm)	
	Glass	Silicon
TZ-F$_{unc}$	76	116
TZ-F$_{1T}$	39	28
TZ-F$_{2T}$	52	51
TZ-F$_{3T}$	63	74

The optical characterization of the films was done using spectroellipsometric measurements. Films thickness was calculated from SE measurements data using Cauchy model. In Table 3 the thickness of the films deposited on the glass and silicon substrate is presented.

In comparison with the as prepared film TZ-F$_{unc}$, the thickness of the thermally treated one obtained after first deposition, as it was expected, decreased significantly. It has to be mentioned that the films with the same number of the layer depositions present thickness that have close values no matter of the substrate nature.

In Fig. 6 (a, b) and 7 (a, b) the refractive indexes (n) and the extinction coefficient (k) for the TZ-F type films deposited on the glass and silicon substrates respectively are presented. The refractive index increases with the number of layers. The data for the one and two layers deposition overlap. The higher refractive index was obtained for the case of TZ-F$_{G3T}$ films n=1.98 (at 300 nm). Similar values of (n: 1.87 -2.15) were reported by Cetinorgu[7] also from SE measurements.

As could be seen in Fig. 6b, low values (close to zero) have been obtained for the extinction coefficient, k, of the TZ-F films deposited on glass, except for the as-prepared films (TZ$_{Gunc}$-maybe due to the presence of some organics) pointing the obtaining of TCO-type films.

The refractive index of the TZ-F type films deposited on the silicon wafer varies between 1.74-1.85 and the extinction coefficients ranged under 0.04 in the 400-800 nm range.

3.2. Characterization of the Zn-Sn-O films with zinc/tin ratio 2:1

In Fig. 8, X-ray diffraction pattern for TZ$_2$-F$_{S4T}$ film with zinc/tin ratio 2:1, deposited on silicon substrate is presented. The incipient crystallisation of the Zn$_2$SnO$_4$ binary compound (ASTM file 74-2184) could be observed.

In Fig. 9 (a, b) the AFM images of TZ$_2$-F$_{4T}$ films deposited on glass and silicon substrate are presented.

A distinctive morphology of the films depending on the type of substrate is observed. From the similar image analyses the grain size of TZ$_2$-F$_{4T}$ films were calculated and presented in Table 4.

Similarly to the noticed features of TZ-F type films, the grain sizes of the TZ$_2$-F type films deposited on the glass substrate are one order of magnitude higher than those deposited on silicon wafer. By comparison to data presented in Table 2, it can be observed that TZ$_2$-F type films on both substrates have grain size larger than TZ-F type films.

Thickness of the film calculated from SE measurements data is presented in the Table 5.

No major difference has been observed between the thickness of TZ$_2$–F type films deposited on silicon wafer and that of the films deposited on silica substrate.

In Fig. 10 (a, b) the refractive index (n) and the extinction coefficient (k) for the TZ$_2$-F type films deposited on the silicon wafer are presented. The films obtained after four depositions on the silicon substrate present the highest refractive indexes **n** of 2.03 to 2.33 and, as expected, the smallest values of extinction coefficient.
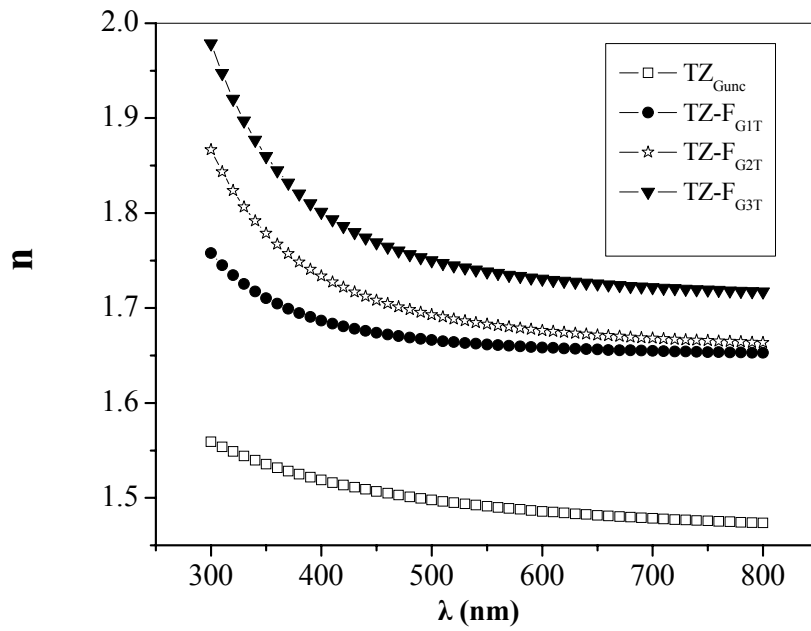
a
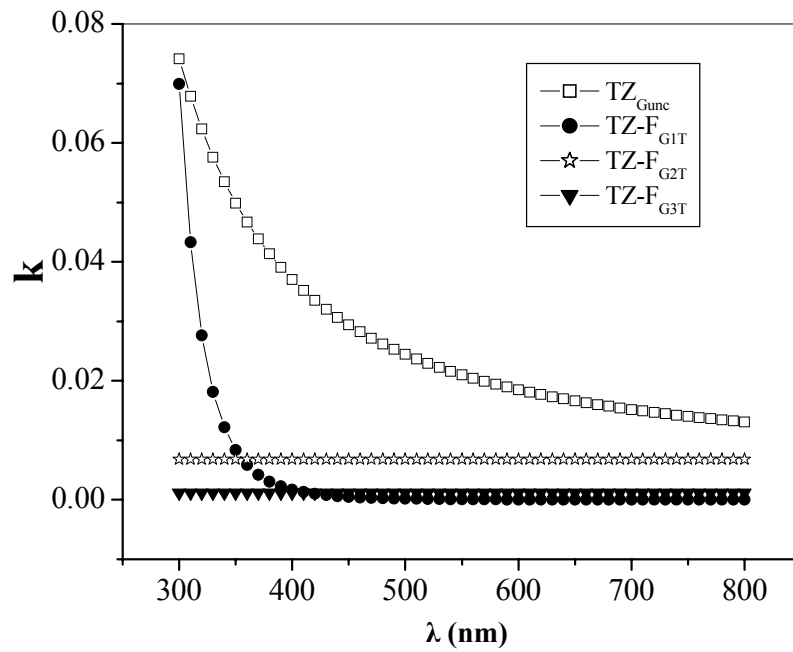
b

Fig. 6 – Optical constants (n, k) of the TZ-F type films deposited on glass substrate: (a) refractive index (n); (b) extinction coefficient (k).
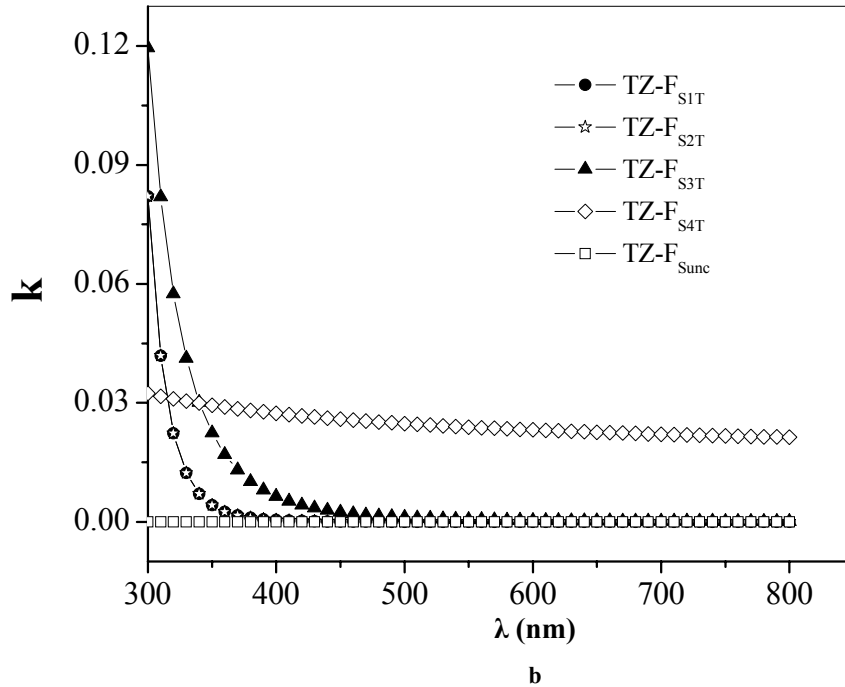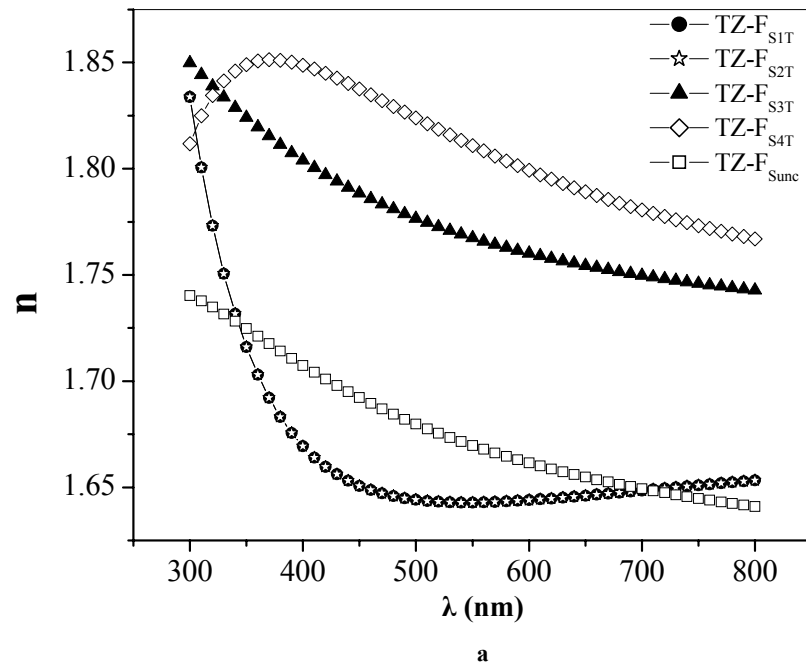
Fig. 7 – Optical constants (n,k) of the TZ-F type films deposited on silicon substrate:
(a) refractive index (n); (b) extinction coefficient (k).

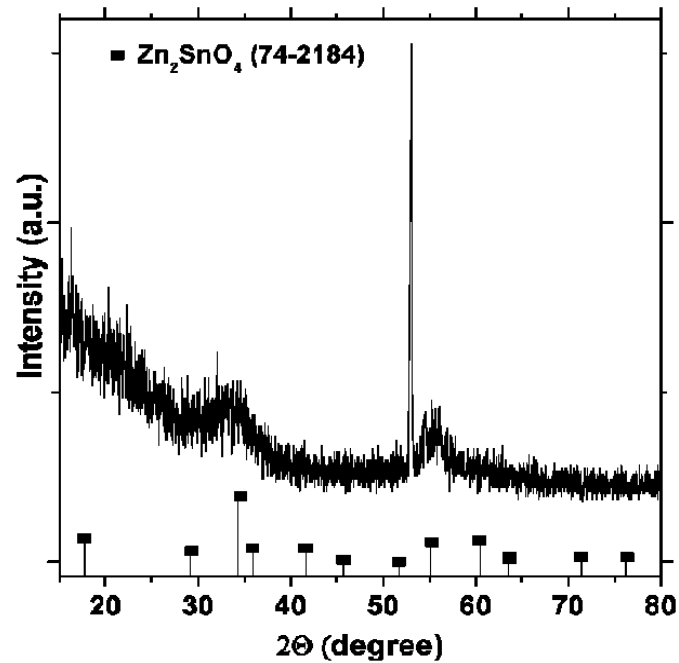Fig. 8 – XRD pattern of Zn–Sn-O film with zinc/tin ratio 2:1, deposited on silicon substrate.

Table 4

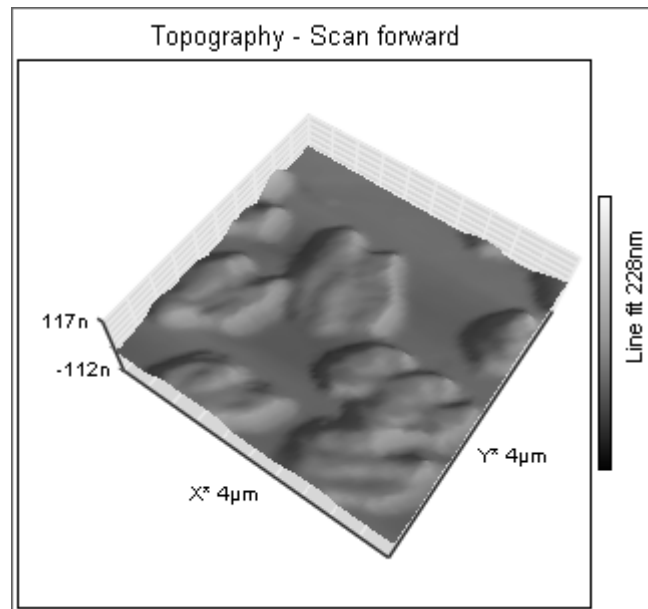Grain sizes of the TZ $_2$-F$_{4T}$ type films deposited on glass and silicon substrate; (L-length; W-width; D- diameter)

ID	Glass support			Silicon support		
	L(nm)	W (nm)	D (nm)	L(nm)	W(nm)	D (nm)
Mean	542	184	354	66	21	42
SD	477	157	303	67	15	35

Table 5

The thickness of TZ$_2$-F type films

Films	Thickness (nm)	
	Glass	Silicon
TZ$_2$-Func	-	107
TZ$_2$-F$_{1T}$	16	37
TZ$_2$-F$_{2T}$	40	51
TZ$_2$-F$_{3T}$	-	90
TZ$_2$-F$_{4T}$	93	124

(a)
RMS = 10.83 nm
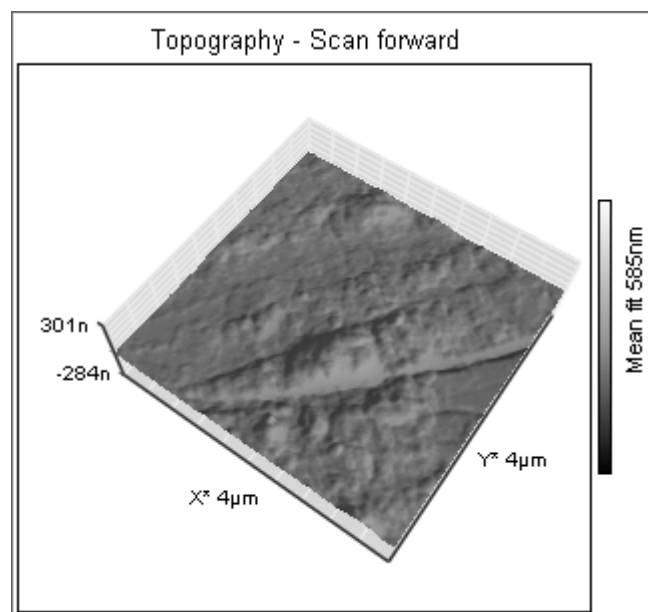
b)

RMS = 3.78 nm

Fig. 9 – 3D AFM images of the TZ_2-F_{4T} films:
(a) deposited on glass substrate (RMS=10.83 nm); (b) deposited on silicon substrate (RMS = 3.78 nm).
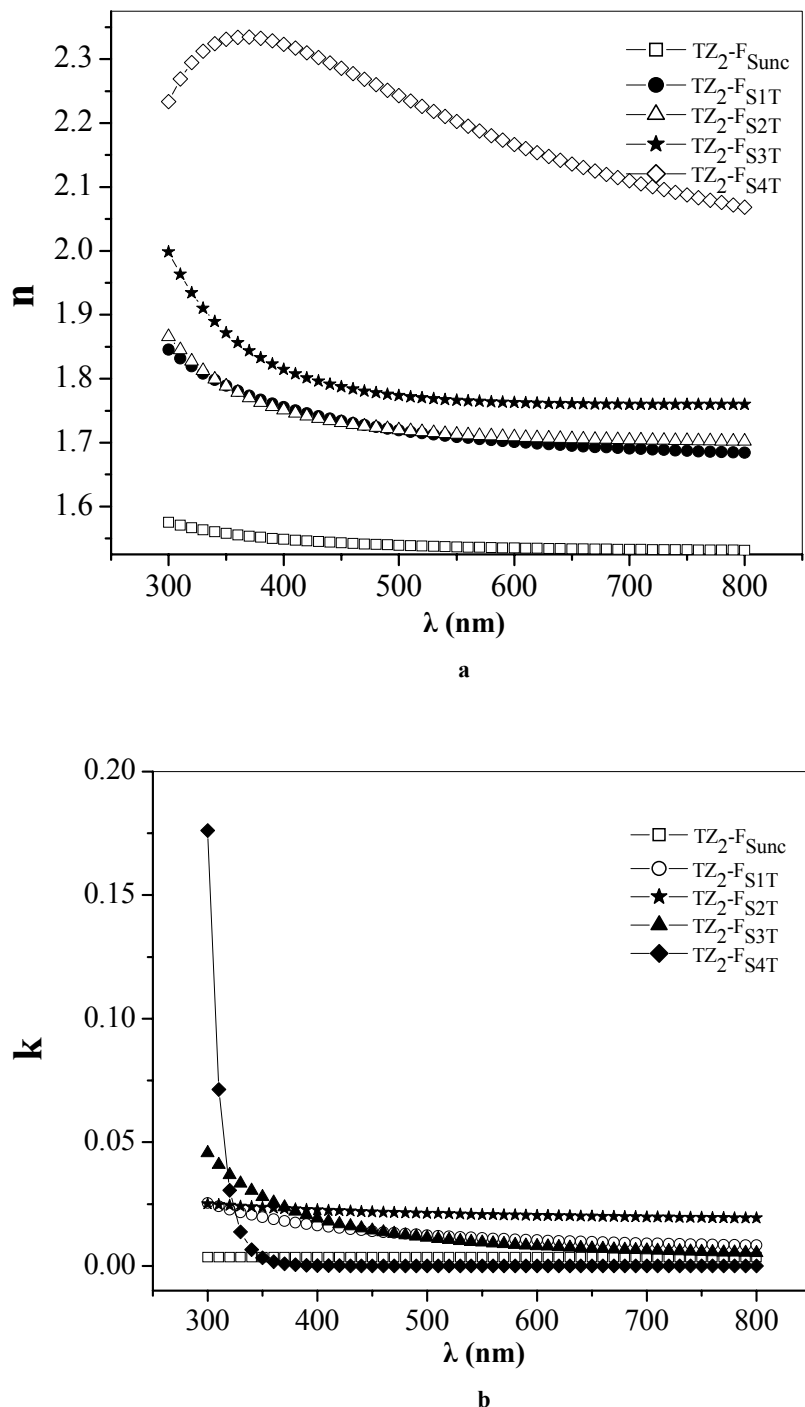
a

b

Fig. 10 – Optical constants (n, k) of the TZ 2-F type films deposited on silicon substrate:
(a) refractive index (n); (b) extinction coefficient (k).

Fluorescence emission spectra of the films deposited on the glass substrate are presented in Fig. 11.

It can be observed that the thermally treated TZ_2–F_{GnT} type films present the main emission bands at about 376 nm, 462 nm and 524 nm, in the same spectral domain as zinc oxide. According to the literature data[21-22] the blue-green band (462 nm) and the green band (524 nm) were observed for Zn_2SnO_4 nanowires.
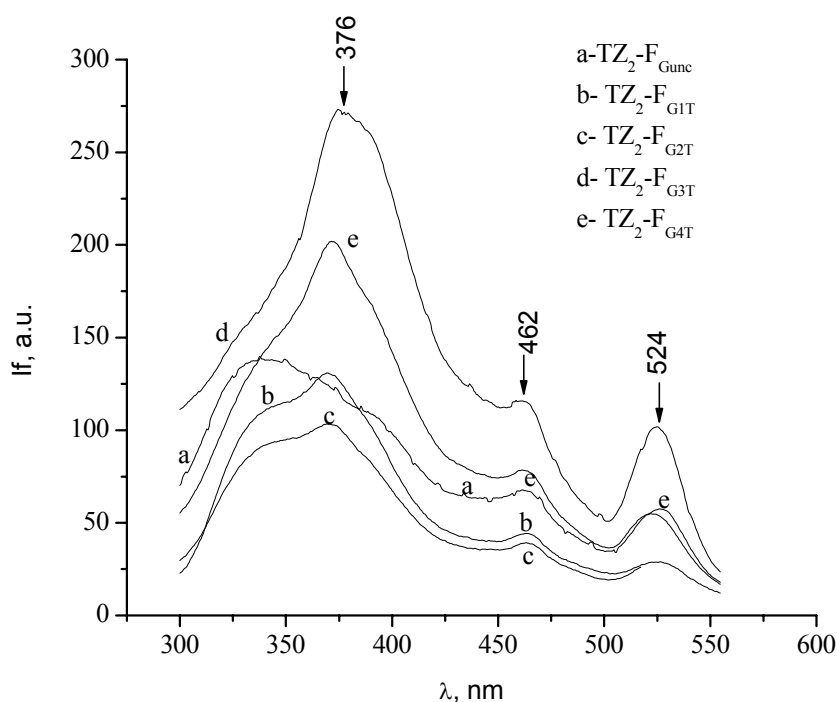
Fig. 11 – Fluorescence spectra of TZ$_2$-F type films on the glass substrate.

CONCLUSIONS

Stable transparent Zn-Sn-O solutions were obtained under soft conditions starting from organic tin and zinc salts in absolute ethylic alcohol, using triethanolamine as chelating agent.

The obtained powders after thermal treatment of the gels at 500 ℃ for one hour are amorphous.

Adherent, continuous and homogenous films deposited on the glass and silicon substrates were obtained by dip coating method.

As evidenced by AFM, the films annealed one hour at 500 °C, developed a distinctive morphology according to the zinc/tin atomic ratio. The grain size calculated from AFM data of both Zn-Sn-O type films with atomic ratio 1:1 and 2:1 deposited on the glass is one order magnitude higher than that of similar films on silicon.

The values of optical constants (refractive index and extinction coefficient), calculated from SE data, are in good agreement with literature data.

All studied samples exhibit fluorescence emission with the main bands depending on their nature (solution or solid state).

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